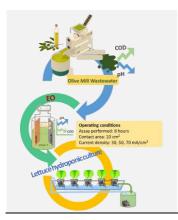
Olive mill wastewater electro-oxidation aiming the utilization of the treated effluent in hydroponic growth of lettuces

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The objective of this work was to study the electrochemical degradation of olive mill wastewater at a BDD anode to obtain a treated effluent with low organic content, but with adequate conductivity and pH that allows its utilization in hydroponic growth of lettuces. The electrochemical assays were run at different applied current densities, varying between 30 and 70 mA cm⁻², during 6 to 8 h. For the lowest applied current density, the most economical process, a reduction in chemical oxygen demand of 74% was observed after 8 h assays. This final treated solution presented a pH of 6.96±0.05 and a conductivity of 1.39±0.06 mS cm⁻¹, while an increase in the biodegradability index from 0.30 to 0.60 was also observed. Thus, the treated OMW presented good characteristics to be utilized as nutritive solution in hydroponic culture of lettuces, contributing to lower water consumption in farming industry.

Introduction

The olive oil industry is one of the oldest and most traditional agro-industrial activities in Mediterranean region, representing a fundamental sector in the structure of agricultural production in these countries, whose climate is favourable for the cultivation of olive trees [1,2]. According to data from the International Olive Council for the 2023/2024 campaign, Mediterranean countries (considering Spain, Algeria, Turkey, Greece, Italy, Tunisia, Morocco, and Portugal) produced 2009 thousand tons of olive oil, which corresponds to 83.5% of world production, with Portugal being the seventh largest olive oil producer in the world (125 thousand tons). Initially, the olive oil production process consisted only of crushing the olives with the addition of water. With technological evolution, the olive oil production process has changed, although the addition of water continues to be present in the washing, blending, and separation stages, which leads to the formation of an effluent - olive mill wastewater (OMW) [2,3]. OMW composition depends on several factors: vegetation and olive water, a result of the variety and maturation of the olive; type of soil; olive harvest season; pesticides and fertilizers used; and climatic conditions [4]. OMW has acidic characteristics (pH between 4.3-5.7), dark color (reddish-brown), intense and unpleasant smell, high electrical conductivity (5.0-8.0 dS m⁻¹), high content in phenols (0.8-9.0 g L⁻¹), chemical oxygen demand (COD) (16.5-192.8 g L⁻¹), bacteria and fungi, sugars, and organic acids [5-7]. Despite its complex composition, OMW, after an appropriate treatment, presents nutrients for crops growth, namely in hydroponic cultivation [8].

Over the years, various technologies have been

considered to treat OMW, from physicochemical, biological, and combined treatment processes [3,4]. Among them, electrochemical technologies present a good option to treat such complex effluents [9]. The objective of this work was to treat an OMW by electrochemical oxidation (EO), at a BDD anode, to have a treated effluent with adequate pH and conductivity to grow lettuces by hydroponics [8].

Material and Methods

OMW samples, before and after the electrochemical experiments, were analysed, according to standard procedures [10], for the following parameters: COD, biochemical oxygen demand (BOD₅) total dissolved organic and inorganic carbon (DOC, DIC), and total dissolved nitrogen (TDN). COD determinations followed the closed reflux titrimetric method. BOD₅ was evaluated through the respirometric method, using a WTW's Oxitop® system. DOC, DIC, and TDN were measured in a Shimadzu TOC-VCPH analyzer combined with a TNM-1 unit. Ions concentration was determined by ion chromatography, with a Shimadzu 20A Prominence HPLC system, equipped with a Shimadzu CDD 10Avp conductivity detector, following the analytical procedure described elsewhere [8]. The pH and the electrical conductivity were measured using a HANNA pH meter (HI 931400) and a Mettler Toledo conductivity meter (SevenEasy S30K), respectively. The turbidity was determined through a Lovibond TB 350 turbidimeter. EO assays were performed in batch mode. The volume utilized in each experiment was 200 mL. Anode was a BDD (10 cm²) and cathode was a stainless steel plate (10 cm²), being the distance between them 0.5 cm. The applied current densities were 30, 50, and 70 mA cm⁻².

Results and Discussion

Table 1 presents the characterization of the OMW utilized in this study. It presents a medium high COD value, with acid pH. The relation between COD and DOC and turbidity points to a partial suspension of the organic matter.

Table 1. OMW physicochemical characteristics.

Parameter	Mean value ± SD ^a
COD / g L ^{_1}	5.90 ± 0.01
BOD ₅ /COD	0.39
DOC / mg L ^{_1}	805 ± 9
DIC / mg L ^{_1}	18 ± 2
TDN / mg L ⁻¹	12.3 ± 0.5
pH	5.41 ± 0.05
Conductivity / mS cm ⁻¹	1.75 ± 0.03
Turbidity / NTU	74 ± 3
^a SD – Standard deviation.	

Figure 1 presents the results of OMW oxidation at a BDD anode. The faster COD decay, when compared to DOC, is due to the organic matter that is not yet dissolved at the beginning of the assay, being measured in COD but not in DOC, since samples for DOC determination are filtered. In all the assays it can be observed an increase in pH. Since the objective is to utilize the treated effluent in lettuce crops by hydroponics, which needs a pH and conductivity between 6–7 and 2.5–5 mS cm⁻¹, respectively, the best results were attained at 30 mA cm⁻². Regarding the biodegradability index, BOD₅/COD, there was an increase to 0.60 for the assay performed at 30 mA cm⁻². Organic nitrogen was mainly converted to nitrate (data not shown).

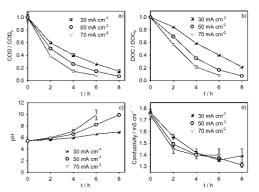


Figure 1. (a) COD and (b) DOC decays, and (c) pH and (d) conductivity variation during OMW degradation assays performed at different applied current densities.

Conclusions

OMW was successfully oxidized at a BDD anode, with COD removals of 74, 85, and 92% after 6-h assays performed at 30, 50, and 70 mA cm⁻², respectively.

Biodegradability index increased during the EO tests, with final results of 0.60 and 0.90 for the applied current densities of 30 and 50 mA cm⁻², respectively.

The most adequate final solution to pursue lettuce hydroponics culture was that obtained at 30 mA cm⁻², regarding pH and conductivity criteria.

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